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PILOT PLANT OPTIMIZATION OF PHOSPHORIC ACID RECOVER PROCESS

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Lancy Laboratories, Incorporated

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A pilot plant study was carried out which demonstrated the effectiveness and economic feasibility of a unique ion exchange process referred to as "acid retardation" for purifying spent phosphoric acid used in bright finishing aluminum parts. A continuous ion exchange system was employed to separate the aluminum contamination from a spent phosphoric acid waste obtained from a manufacturing plant. The anion resin accomplishes the separation by retarding the phosphoric acid as the processing solution flows through the bed. The aluminum remains in the waste solution and passes out of the column in the effluent. The acid is then eluted from the bed with water, eliminating the use of chemicals which are needed to regenerate the resin in conventional ion exchange systems.

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The National Environmental Research Center--Cincinnati has reviewed this report and approved its publication. Approval does not signify that the contents necessarily reflect the views and policies of the U. S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research centers provide this multidisciplinary focus through programs engaged in

studies on the effects of environmental contaminants on man and the biosphere, and

a search for ways to prevent contamination and to recycle valuable resources.

The studies for this report were undertaken to optimize and evaluate the economics of a new acid regeneration process which permits the recovery of phosphoric acid used in the bright finishing of aluminum. The unique waste treatment process uses sorption, a physical process, rather than chemicals, to effect separation of the valuable acid from contaminating metal salts. This closed-loop type of approach prevents pollution of the water environment by purifying the contaminated phosphoric acid for reuse in the bright finishing operation.

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ABSTRACT

A unique process for separating strong acids in aqueous solutions from their associated metal salts has been developed by Lancy Laboratories. Based upon preliminary pilot plant tests, the Douglas & Lomason Company applied for EPA support on a project to demonstrate the application of the new technique for reclaiming phosphoric acid used in the bright finishing of aluminum.

Phase I of the resultant project included improvement and optimization of the process in a pilot plant contactor and detailed studies of the economic feasibility of the proposed commercial installation. The pilot work indicated that with feed streams ranging from 25-35% phosphoric acid content, at least 75% of the H_3PO_4 fed to the contactor could be recovered and returned to the bright dip tank.

Projections for the commercial installation, based upon pilot plant data, show that the required investment capital can be returned in 1.5 years or less when both the recovered acid volume and the obviated waste treatment costs are considered. For those plants returning 35% waste acid to their supplier, the additional savings generated by the recovery system will return the investment in approximately two years.

The new waste treatment process has considerable potential for controlling environmental problems based on the significantly reduced waste treatment costs and sludge production achieved in the pilot plant study, as well as its widespread application to other strong acid wastes.

This report was submitted in fulfillment of Project S802637 by the Douglas & Lomason Company under the partial sponsorship of the Environmental Protection Agency.

CONTENTS

		Page
Abstract		iv
List of Figures		vi
List of Tables		vii
Acknowledgements		viii
Sections		
I	Conclusions	1
II	Recommendations	2
III	Introduction	3
IV	Optimization Study	9
V	Feasibility Study	19
VI	References	27

FIGURES

No.		Page
1	Schematic Flow Diagram for Recovery Process	8
2	Photograph of Pilot Plant	10
3	General Arrangement of Recovery System	21

TABLES

No.		Page
1	Pilot Plant Operating Data	12
2	Pilot Plant Operating Data	13
3	Pilot Plant Operating Data	14
4	Pilot Plant Operating Data	16
5	Pilot Plant Operating Data	17
6	Summary of Capital Costs	22
7	Estimated Direct Annual Operating Costs	24

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Assistance in gathering data on the operating costs, chemical consumption, and production loads at the Cleveland works of Douglas & Lomason was provided by Mr. Harry A. Lomason, Mr. Charles A. Parker, Mr. G. Lyndon Milek, and Mr. S. D. Cramer, all of the Douglas & Lomason Company.

The operation of the pilot plant, design of the recovery system, and preparation of this report were supervised by Leslie E. Lancy, Ph.D., of Lancy Laboratories, Division of Dart Industries, Inc., Chemical Group, Zelienople, Pennsylvania. The pilot plant operation and collection of data, and the design of the full-scale recovery system were directed by Mr. James H. Weet of Lancy Laboratories. The report was prepared by Mr. F. A. Steward, also of Lancy.

The advice and cooperation of Mr. John Ciancia, Project Officer and Chief of the Industrial Pollution Control Branch, Industrial Waste Treatment Research Laboratory--NERC Cincinnati, EPA, is acknowledged with sincere thanks.

This report was submitted in fulfillment of Project No. S802637 under the partial sponsorship of the Environmental Protection Agency, United States of America.

SECTION I

CONCLUSIONS

1. In an aluminum bright dipping operation, the projected acid regeneration and recovery system will significantly reduce the consumption of both process and waste treatment chemicals and can generate sufficient savings to return the required investment in a relatively short time.

2. Based upon pilot plant performance, it is anticipated that a full-scale, 24" dia. contactor can separate the aluminum from 1,752 gal. (6,624 l) per day of 35% feed liquor, with at least 75% recovery of the input H_3PO_4. This level of recovery corresponds to savings of $166,000/year in raw purchased acid at the current rate of $218.40/ton of 80% phosphoric acid.

3. Comparison of the in-house recovery technique with return to the supplier of 35% waste acid, as currently practiced at many large plants, indicates that invested capital can be returned in about two years with the additional savings.

4. Demonstration of the proposed commercial installation will make available to the metal finishing trade an important tool for reducing consumption of raw materials and costs, and greatly reducing the environmental impact associated with operation of acid solutions used to bright dip, clean, or pickle metals.

SECTION II

RECOMMENDATIONS

Phase II of the demonstration project should be undertaken to bear out the efficacy of the recovery system under full-scale plant operating conditions. This Phase will cover one year of operation and will result in factual data on the economics of the process.

Potential market opportunities for the by-product aluminum phosphate solution should be explored and compared. There will undoubtedly be some industry which can use this material as an input to their process, thus eliminating waste treatment and sludge generation, and offering additional economic return.

Investigation on the applicability of the sorption technology to other commercial acid regeneration processes should be pursued.

SECTION III

INTRODUCTION

As a manufacturer of hardware, accessories, and trim for the automobile industry, the Douglas & Lomason Company produces bright trim for automobile bodies in its Cleveland, Mississippi plant, by stamping aluminum into shape and giving the surface a bright corrosion-resistant finish. In the finishing operation, the parts are immersed in a bright dip which is a mixture of phosphoric and nitric acids that chemically polishes the surface of the aluminum, giving a bright, highly reflective surface. After rinsing, the parts go through a sulfuric acid anodizing process to develop a durable protective anodic coating.

This type of bright finishing process is common in the aluminum industry, and all commercial bright dipping operations utilize a solution based on phosphoric acid. It is estimated that approximately 45,000 tons of phosphoric acid are consumed annually in the United States for such aluminum bright dipping operations. The operating cost for the bright dip is a significant part of the total aluminum finishing cost because phosphoric acid is a relatively expensive chemical, and the process is rather inefficient. Since the bright dip solution must be operated at a high acid concentration (60-80%), it has a high viscosity, rather like a thick syrup. Furthermore, the parts must be moved quickly from the bright dip solution into a subsequent rinse so as to stop the attack of the surface film as quickly as possible, to avoid etching which dulls the surface appearance. The high viscosity and rapid transfer requirements combine to create extremely high drag-out of the bright dip solution on the product. In practice, this means that only 10-15% of the purchased phosphoric acid added to the bright dip is actually consumed in chemically polishing the surface. The remainder is lost to the subsequent rinses.

In addition to being an expensive operation, the bright dipping of aluminum generally creates a serious waste water disposal problem. Since phosphate is a nutrient ion and should not be discharged to surface waters, lime must be used for neutralization of the rinse waters. This neutralization creates large volumes of calcium phosphate sludge which is low in dry solids. One pound of H_3PO_4 in a dilute rinse water stream will produce 30-50 pounds of wet, gelatinous sludge requiring dipsosal. A

typical method for disposing of such waste slurries is to build a series of lagoons on the plant property, but this is obviously not a long-term solution.

Current Practice

The Cleveland, Mississippi plant reduces their waste discharge and recoups a portion of the value of the acid lost from bright dipping by operating a series of three recovery rinses following the bright dip. These are operated in a countercurrent fashion, with fresh water input to the third rinse, and a very slight overflow on the first (most concentrated) rinse going to a storage tank. The flow rate of the rinse series is controlled so as to maintain 35% acid in the tank overflowing to storage. The accumulated 35% acid is hauled by tank truck to a fertilizer manufacturer and the plant is reimbursed approximately 36% of the full value of the phosphoric acid content.

This recovery by sale to a by-product user is not uncommon in the industry, and is an improvement over complete wastage. However, considerable improvement could be made by returning the acid to the bright dip solution, thus recovering 100% of the initial acid value, and eliminating dependence on the needs of a by-product user. Such a recycling operation requires an economical method for separating the aluminum phosphate formed by the chemical polishing reaction from the remaining free phosphoric acid.

New Approach

Recognizing the requirement in the aluminum finishing industry, Lancy Laboratories undertook research and development work on a process which would separate aluminum phosphate and phosphoric acid, relying on an empirically-observed and theoretically explainable paradox, called by the inventor, "acid retardation."[1] This ingenious observation is based on the fact that acid is retarded, or held back, when a solution containing both a strong acid and its salts is passed through a column of strong base anion exchange resin, but has never been demonstrated earlier on a pilot plant or commercial scale. The mechanism appears to be a purely physical adsorption with the entire acid molecule being preferentially adsorbed to the exclusion of the acid salts. Probably the most significant advantage of the acid retardation technique is that the acid molecule can be

desorbed from the resin by washing it with water. The resin surface, now freed of the adsorbed acid, is ready for the next loading sequence, allowing repeated usage of the resin solid as an adsorber.

To obtain maximum efficiency from the acid retardation principle, it is necessary to use a continuous, countercurrent contactor to expose the resin bed to both feed and stripping solutions. This permits the metal salt stream (aluminum phosphate) to be drawn from the column continuously at maximum salt and minimum free acid concentration. Likewise, the product acid can be continuously withdrawn at its maximum concentration and with minimum contamination by aluminum. This greatly reduces the equipment and energy required for evaporating the acid before returning it to the bright dip. The most important feature of such contactor design is naturally the avoidance of mixing of the zones of significantly different solutions of acid and metal salt content. Another important aspect is the avoidance of undue dilution of the acid to be reclaimed.

As part of the development program, Lancy Laboratories constructed a pilot plant contactor device, designed specifically for the adsorption-desorption process. Early runs on the pilot plant showed encouraging results and indicated that further development work was justified.

Background

An earlier approach to recovery of similar bright dip acid employed a continuous pulsed ion exchange column, but the mechanism of acid-salt separation was conventional ion exchange. A cation exchange resin removed aluminum ions from the waste acid stream, and was subsequently regenerated with sulfuric acid. At least one commercial installation[2] using cation exchange is in operation, but the chemical, operating, and maintenance costs offset the value of the recovered acid. The acid retardation approach has an important advantage in that there is no chemical consumption in the operation.

The requirements for a contactor for the new adsorption process were different than for the existing ion exchange systems. The new contactor, aiming for a physical adsorption and desorption, had to be developed, and is covered by the patent application

bearing U. S. Serial Number 241,639. This system accurately measures the volume of the various feed streams so as to consistently maintain the necessary balance in the contactor with a minimum of mixing and dilution in the zones of differential concentration and no operator attendance.

Construction of the first pilot plant configuration was followed by an extensive period of evaluation during which various aspects of the electrical, mechanical, and hydraulic design were modified to obtain optimum economy in operation. From the reasonably stable, promising preliminary pilot-scale demonstration runs, progress was made to a more dependable, stable operating system with significantly improved economical justification to the point where the refinements accomplished in the pilot stage allowed dependable predictions for the consideration of a full-scale commercial installation.

Demonstration Grant

Since the process is unique, an Application for Federal Assistance with the proposed prototype installation was filed with the U. S. Environmental Protection Agency. It was proposed that the demonstration project be conducted in two phases.

Phase I would be a Process Optimization and Feasibility Study. During this phase, the operation of the pilot plant would be tailored to a feed stream simulating that which is available at the Cleveland, Mississippi plant, so as to determine the operating condition which would give maximum efficiency and recovery of the wasted acid. After the Optimum Conditions had been determined, it was planned that a sample of feed liquor from the Cleveland plant would be processed on the pilot plant over a period of at least a week to insure consistent and repeatable results. The Feasibility Study was to be primarily an economic analysis considering the quantities of waste acid available at the Cleveland plant, the capital investment required for a suitable contactor installation, the continuing operating and maintenance costs for the recovery facility, and the value of the recovered acid. Based upon the results of this analysis, it could be decided whether to proceed with the prototype installation.

Phase II of the proposed demonstration project would cover the construction and installation of the prototype recovery system at the Cleveland, Mississippi plant, and documentation of the first year's operating experience and operating and maintenance costs. Figure 1 shows a schematic representation of the new phosphoric acid recovery process.

Because of the potential environmental significance of the process in permitting recycling of common metal finishing acid solutions, the EPA indicated an interest in participating in the project. Approval for Phase I of the grant was received covering a three-month period. A final report on the entire demonstration will be written after one year of full-scale operation.

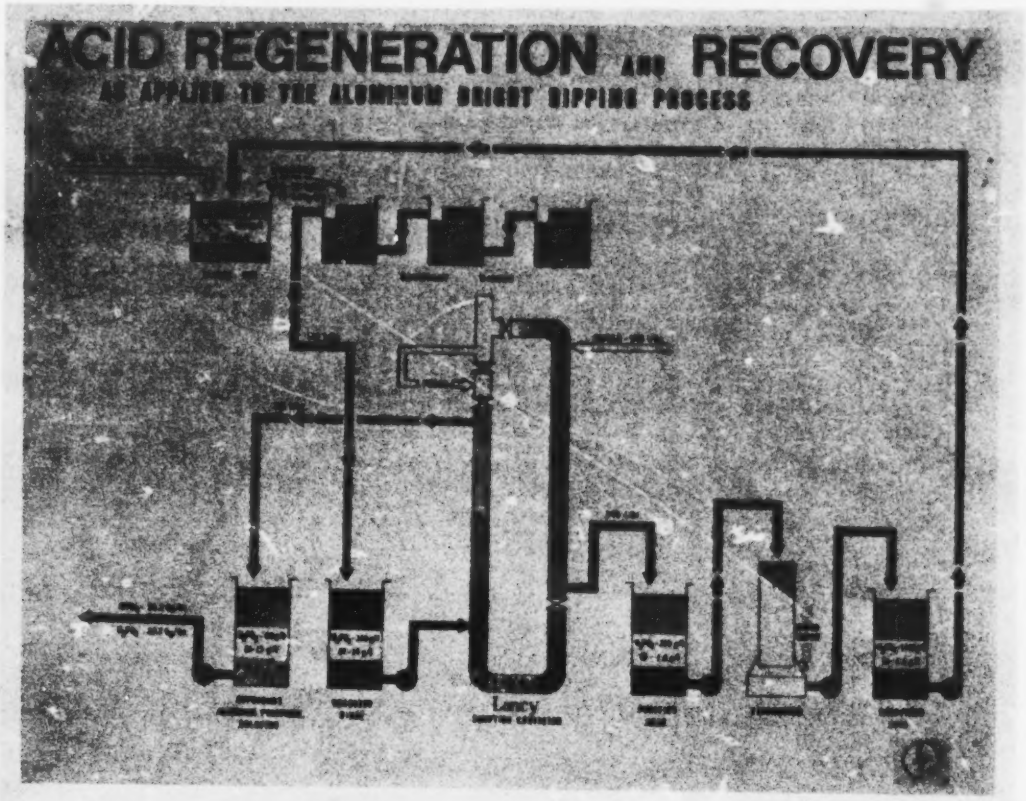

Figure 1. Schematic Flow Diagram for Recovery Process

IV. OPTIMIZATION STUDY

One of the first tests done during the grant period was to compare the effectiveness of various resins as an adsorption medium under laboratory static column conditions. On the basis of these tests, it was determined that Dowex SBR-P resin showed the best overall characteristics for the process. The adsorption capacity was equal to or better than the other resins tested, and the superior hydraulic and mechanical characteristics which are extremely important in a moving-bed contactor, were a decided advantage. Therefore, the pilot plant was charged with the Dowex resin to begin the grant period tests.

Figure 2 is a picture of the pilot plant contactor used for the tests. With the exception of the diameter of the resin loop tubing, and the size of the pumps and reservoir tanks, it is identical to the commercial unit contemplated. The control system is for all practical purposes identical. The pilot unit is constructed with 2" dia. Pyrex glass pipe as the resin loop, giving a cross-sectional area of 3.14 sq. in. (20.26 m^2). The rate of introducing both feed liquor and stripping water varied during the tests between 0.40 gal./hr. (1.5 liter per hour) and 0.66 gal./hr. (2.5 liters per hour), giving a bed flux rate in the range of 0.13 gal./hr. - square inch (0.074 liters per hour - square centimeter) and 0.66 gal./hr. - square inch (0.123 liters per hour - square centimeter). The resin bed in the sorbtion contactor is periodically pulsed hydraulically so as to move it an increment (approximately 10 inches - 25.4 cm) in a counterclockwise direction around the resin loop. Between these pulses, the resin valves close, dividing the contactor loop into a loading and stripping zone. In these areas, the liquid flow progresses opposite to the direction of resin movement (clockwise). Thus, the net effect is an approximation of continuous countercurrent flow of the resin bed and the liquid feeds. Ideally, the best approximation would be obtained by very small incremental pulses made frequently. However, the frequency of the pulses is limited by the mechanics of the contactor operation, since a given number of functions, each requiring time, must occur between each pulse. Thus, assuming that the pulse frequency is fixed, the only variable permitting adjustment of the contactor capacity is the stroke length. Increasing the stroke length moves more resin around the loop per unit of time, thus tending to increase the capacity of the unit. However, this tendency is opposed by the facts that:

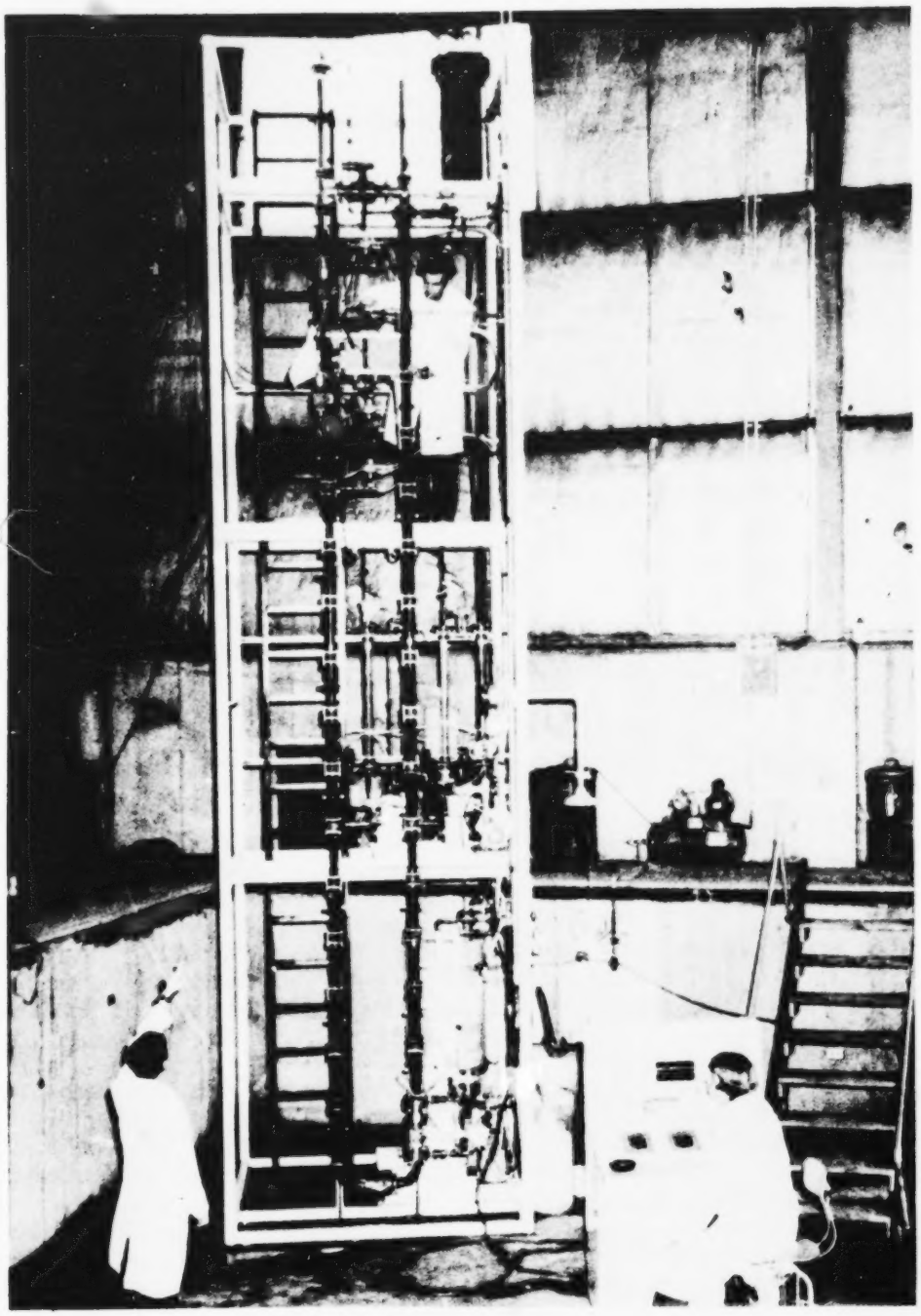

Figure 2. Pilot Plant

(1) The adsorption reaction is time dependent; and

(2) The turbulence during pulsing causes mixing along the length of the sections, thus disturbing idealized equilibrium conditions.

Previous pilot plant work had established that the stroke length employed was a reasonable compromise between capacity and separation efficiency.

Table 1 shows the data obtained during the initial pilot runs in the grant period.

A change was made to permit warm water to be used in the stripping section, as some rough laboratory tests had indicated that it would more thoroughly strip the resin in the same amount of time, thus giving a small improvement in the capacity of the resin as it entered the loading section. To avoid exceeding the temperature tolerance of the resin, the temperature of the strip water was held at 120° F (49° C). Table 2 gives the operation data obtained over several days of operation following this modification. The increase in acid recovery efficiency may be directly attributed to the increased capacity of the resin.

A study of the previous operating data led to the conclusion that longer contact time in the loading section should further increase the amount of acid adsorbed on a unit volume of resin, thus increasing the rejection of aluminum, and the recovery of acid at the same aluminum contamination level. Two additional sections of pipe were added to the loading section increasing its length by two feet (0.61 m). As can be seen from the data in Table 3, the anticipated improvement in acid recovery was realized.

As explained earlier, one of the most important aspects of the contactor design is maintaining extremely accurate control over the input of pulse and counterpulse liquid. Since water under pressure is used to move the resin bed, there is a natural slippage of the water through the porous bed, and the volume of slippage is dependent on the condition of the bed. Since the amount of undesirable particulate matter and the compaction of the bed can vary from hour to hour, it is essential that the volume of the slippage be measured and precisely opposed by the counterpulse volume. The method of accomplishing this is described completely in the previously-referenced patent application, and it will be seen that two differential pressure controllers are key components in the system.

Table 1

Pilot Plant Operating Data

Date	Time	Feed Stream			Waste Stream			Product Acid			Acid Recovery	Aluminum Removal
		l/hr.	Al g/l	H_3PO_4 g/l	l/hr.	Al g/l	H_3PO_4 g/l	l/hr.	Al g/l	H_3PO_4 g/l		
8/2/73	0300	1.5	16.3	270	1.75	16.5	88.2	1.5	2.3	245		
	0900	2.0	16.3	270	2.0	17.0	78.5	2.0	2.5	244		
	1400	1.9	15.9	285	2.25	14.5	73.5	1.9	1.9	245	73.0%	89.0%
8/3/73	0300	2.0	16.6	343	3.25	10.9	49	1.5	2.0	245		
	0700	2.0	16.6	343	3.25	12.1	49	1.5	1.3	240		
	2000	1.9	18.5	353	2.5	13.8	23.5	1.6	0.8	221	67.5%	93.0%
8/6/73	0300	1.6	15.8	338	1.75	13.3	78.4	1.5	.75	196		
	0900	1.5	15.8	338	1.6	13.8	64.5	1.5	1.25	230		
	1600	1.5	20.1	358	1.5	17.1	83.0	1.4	2.5	235	62.5%	91.5%
8/7/73	0900	1.7	17.8	348	2.75	11.3	58.8	1.32	0.8	250		
	2300	1.5	17.8	348	1.40	16.4	78.4	1.42	1.6	235		
	0800	1.8	17.8	348	1.5	15.5	68.5	1.4	1.7	226	64.0%	92.0%
8/8/73	0400	1.4	17.8	348	1.35	17.8	98	1.2	2.3	281		
	0700	1.5	17.8	348	1.5	15.7	98	1.25	2.3	260		
	0900	1.9	17.8	348	2.3	16.1	87.3	1.3	2.7	271	58%	89%
8/9/73	1600	1.4	17.0	353	1.35	16.1	88.2	1.25	1.7	230		
	2300	1.4	17.0	353	1.29	16.7	98	1.30	1.8	216		
	0400	2.0	15.4	343	1.9	14.5	98	1.6	1.4	260	72.0%	90.0%

Table 2

Pilot Plant Operating Data

Date	Time	Feed Stream			Waste Stream			Product Acid			Acid Recovery	Aluminum Removal
		l/hr.	Al g/l	H_3PO_4 g/l	l/hr.	Al g/l	H_3PO_4 g/l	l/hr.	Al g/l	H_3PO_4 g/l		
8/16/73	1300	1.9	15.7	343	1.9	2.6	15.3	1.85	2.6	230.3		
	1600	2.0	15.7	348	1.8	1.8	14.7	1.80	1.8	215.6		
	2000	2.0	15.7	343	2.0	1.7	14.9	1.90	1.7	264	67%	88%
8/17/73	0900	2.2	15.4	343	2.3	14.7	93	1.6	1.3	260		
	1200	2.2	15.4	343	1.9	13.6	93	1.6	1.8	304		
	0300	2.0	16.5	348	2.0	10.9	49	1.7	2.9	269	69%	93.0%
8/20/73	0730	2.0	15.4	343	1.75	10.5	49	1.75	1.8	318.5		
	1200	1.9	15.4	343	1.80	11.8	54	1.80	2.0	250		
	1630	2.0	15.4	343	1.95	12.8	64	1.80	2.8	249	71%	87.5%
8/21/73	0900	1.8	16 5	348	2.0	5.3	63.7	1.63	2.9	305		
	1400	2.1	16.5	348	3.4	11.7	63.7	1.54	2.4	289	76.5%	84.0%
	0500	2.1	16.5	348	3.75	12.4	68.6	1.80	1.4	225		
8/28/73	1300	2.1	16.5	348	1.58	10.1	54	1.5	1.3	304		
	1600	1.8	16.5	348	1.83	9.3	49	1.73	2.6	299		
	1600	2.0	18.3	343	1.65	15.1	98	1.65	1.6	294	76.5%	91.0%

Table 3

Pilot Plant Operating Data

Date	Time	Feed Stream			Waste Stream			Product Acid			Acid Recovery	Aluminum Removal
		l/hr.	Al g/l	H_3PO_4 g/l	l/hr.	Al g/l	H_3PO_4 g/l	l/hr.	Al g/l	H_3PO_4 g/l		
9/7/73	1900	2.0	18.3	343	1.65	15.6	98	1.75	1.8	290		
	2200	2.0	18.3	343	1.75	15.9	78.5	1.75	1.7	294	81.5%	90.0%
9/11/73	0800	2.5	16.6	490	2.0	16.8	117.5	1.8	1.5	392		
	1000	2.0	16.6	490	1.9	17.3	122.5	1.75	1.3	416		
	1200	2.1	16.6	490	1.5	16.5	112.5	1.75	1.7	441	77.5%	91.0%
	1030	1.5	16.8	490	1.3	17.0	172	1.25	2.1	396		
9/12/73	1130	1.8	17.2	490	1.8	18.4	98	1.8	1.7	360		
	1330	2.0	17.2	490	1.7	18.4	98	1.8	1.9	375		
	1530	2.0	17.2	490	1.8	18.1	113	1.8	1.7	368	69%	92.5%
9/14/73	1230	2.0	16.8	490	1.3	16.9	147	1.30	2.2	430		
	1430	2.0	16.8	490	1.6	17.3	117	1.30	2.1	470		
	1500	2.4	19.1	343	1.8	15.9	733	1.85	1.4	2.85	73%	90%

Repeated observation of the liquid level in the measuring tanks for the pulse and counterpulse water indicated that the desired precision of measurement was not being obtained. The trouble was traced to the mechanical differential pressure switches which were being used to compare liquid levels in these tanks. After numerous attempts to improve the operation of these switches, it was concluded that the inherent limitations of a mechanical switch were an insurmountable obstacle. Therefore, electronic differential control instruments were installed. The transducers at the measuring tanks transmit a milliamp signal to electronic controllers in the master console, allowing extremely precise and repeatable control points to be held.

This control system change was the most significant improvement arising from the pilot plant operation, since it gave the double benefit of improved acid recovery, and greatly reduced operator attendance. Previously it had been necessary to make several adjustments each day to ensure that the various liquid phases were properly positioned in the contactor. Minor variations between these adjustments obviously led to inefficiencies and loss of acid recovery. After installation of the electronic control system, it was found that little or no operator adjustment was required, even after days of continuous operation. Thus, it is assumed that one operator inspection per 24-hour period will be adequate for maintaining the desired balance in the full scale system. Table 4 shows the results of several days of operation at an average acid recovery close to 78%.

Close examination of the entire control system indicated that a number of seconds could be eliminated from many of the functions occurring between pulses. The greatly increased response time of the electronic differential pressure controllers also allowed a time savings. As a result, adjustments were made in the program at the control cabinet, so as to reduce the amount of time required between feed cycles. The net result was an approximate 25% increase in the amount of resin pulsed per hour, permitting an increase from the previous average feed rate of 0.40 gal./hr. (2.0 liters/hour) to 0.66 gal./hr. (2.5 liters/hour) with maintaining near 75% efficiency of acid recovery. Table 5 gives the pertinent data from a number of days of operation at the higher feed rate.

Table 4

Pilot Plant Operating Data

Date	Time	Feed Stream			Waste Stream			Product Acid			Acid Recovery	Aluminum Removal
		l/hr.	Al g/l	H_3PO_4 g/l	l/hr.	Al g/l	H_3PO_4 g/l	l/hr.	Al g/l	H_3PO_4 g/l		
9/25/73	1700	2.3	19.1	343	1.9	14.5	73.5	2.0	1.8	324		
	1900	2.0	19.1	343	2.0	16.1	73.5	2.0	2.1	304		
	1300	2.1	15.7	345	1.9	12.6	78.5	1.8	1.4	294	81.0%	89.0%
9/26/73	1500	2.1	15.7	345	1.8	11.9	73.5	1.8	1.4	294		
	1700	2.0	15.7	345	1.9	11.1	73.5	1.8	1.4	294		
	1100	2.2	15.7	345	2.2	12.0	68.5	2.0	1.4	270		
9/27/73	1400	1.8	15.7	345	1.9	10.7	68.5	1.8	1.7	270		
	1700	1.8	15.7	345	2.0	11.0	68.5	2.0	1.9	270		
	1600	2.0	18.5	490	1.8	14.7	98	2.0	1.4	392	80.5%	89.0%
10/2/73	1400	2.0	15.9	490	1.8	15.6	117.5	2.0	1.5	345		
	1600	2.0	15.9	490	1.7	15.9	117.5	1.8	1.7	345		
	1800	2.0	15.9	490	1.8	16.5	117.5	1.9	1.8	357	69%	90%
10/3/73	1900	2.2	18.5	490	1.8	14.9	98	2.0	1.4	392		
	2100	2.0	18.5	490	1.8	15.0	98	2.0	1.6	392		
	1200	2.0	12.3	392	2.0	11.0	73.5	2.0	1.5	392	82%	90%
10/4/73	1400	2.2	18.5	490	2.2	13.6	78.5	1.85	2.2	392		
	1600	2.3	18.5	490	1.9	13.1	78.5	2.0	1.9	392		
	1800	2.1	18.5	490	1.9	13.9	78.5	2.1	1.9	392	77%	90%
10/5/73	1500	2.1	12.3	392	2.0	11.4	73.5	2.0	1.5	245		
	1700	2.0	12.3	392	2.0	11.6	73.5	2.0	1.4	250		
	1200	2.3	10.9	353	1.9	8.8	58.8	1.9	1.4	216	77%	88%

Table 5

Pilot Plant Operating Data

Date	Time	Feed Stream			Waste Stream			Product Acid			Acid Recovery	Aluminum Removal
		l/hr.	Al g/l	H_3PO_4 g/l	l/hr.	Al g/l	H_3PO_4 g/l	l/hr.	Al g/l	H_3PO_4 g/l		
10/11/73	1400	2.7	10.9	353	2.3	8.9	58.8	2.0	1.3	245		
	1600	2.5	10.9	353	2.2	8.9	68.6	2.1	1.4	260		
	0900	2.5	10.0	343	2.3	8.5	78.4	1.9	1.6	274	79%	87%
10/15/73	1000	2.5	10.4	363	2.2	8.5	117.6	2.1	1.5	289		
	1400	2.5	10.4	363	2.2	8.4	112.5	2.0	1.5	289		
	1800	2.5	10.4	363	2.4	8.5	112.5	2.1	1.5	289	68%	88%
10/16/73	1100	2.5	10.0	343	2.3	8.6	78.4	2.0	1.5	274		
	1300	2.6	10.0	343	2.3	8.1	78.4	2.0	1.3	274		
	1200	2.5	10.5	363	2.3	9.6	78.4	2.35	1.7	304	75%	87%
10/17/73	1000	2.6	10.0	363	2.4	8.6	98	2.0	1.6	309		
	1300	2.4	10.0	363	2.3	8.6	98	2.0	1.5	309		
	1600	2.5	10.0	363	2.5	8.6	98	2.2	1.5	309	72%	87%
10/18/73	1400	2.5	10.5	363	2.3	9.5	88.2	2.30	1.4	284		
	1800	2.5	10.5	363	2.3	9.4	88.2	2.50	1.5	284	79%	86%

One recurring mechanical problem with the operation of the pilot plant was failure of the automatic valves in the various feed and take-off lines connecting to the resin loop. Precise control of the volumes entering and leaving the pressurized resin loop, and thus the overall process balance, requires that these control valves open and close rapidly, and that their shut-off be absolutely leak-tight.

PVC-body, Teflon-faced diaphragm-type valves were used in the original pilot plant construction. In order to assure the necessary rapid, leak-tight shut-off of the diaphragm valves, a rather high operating air pressure was required. Because of this high pressure, a valve which remained in the closed position for any period of time developed a deep imprint on the diaphragm face, resulting in premature failure. Tests with a number of alternate diaphragm materials gave only marginal improvement. As a result, early in the grant period, the automatic valves were replaced with stainless steel body, Teflon-sealed plug valves with pneumatic operators. Shut-off on these was extremely rapid, and completely leak free, and inspection of the units after three months of nearly continuous operation showed no noticeable wear. In view of the fact that the contactor system includes twenty automatic valves, evaluation of the plug valves was an important step in assuring reliable performance of the full-scale installation.

V. FEASIBILITY STUDY

Determination of the feasibility of constructing the full scale contactor system required that accurate cost figures be obtained for the assembly and installation of the equipment. Such figures could only be obtained by doing a detailed design on the full scale contactor and obtaining quotations on the supply of the raw materials and on the necessary welding and fabrication work required for the stainless steel contactor loop, the evaporator, and the structural steel support tower. Quotations were also required on all accessory equipment, such as tanks, pumps, heat exchangers, controls, valves, and piping.

Early in the grant period, design was started on a full scale contactor, based on a resin loop of standard 24" dia., Schedule 10 stainless steel pipe, having an actual inside diameter of 23.5" (59.69 cm). This size was chosen because the single existing anodizing line at the manufacturing plant was generating 1350 gallons (5,110 liters) per day of 35% waste phosphoric acid. The 24" column has a cross-sectional area of approximately 434 sq. in. (2,800 cm^2) which is 138 times that of the pilot unit. Based upon a normal capacity of 2 liters per hour for the pilot plant, the indicated capacity of the 24" unit is 73 gal./hr. (276 liters/hr.) for a total daily throughput of 1,752 gallons (6,624 liters). Use of the next smaller standard size pipe (22") would have given only marginal capacity when calculated by this method. Conservative design requires that a safety factor be allowed when scaling up from the pilot plant results. For example, distribution is one of the problems encountered when going to larger cross-sectional areas. Design of the in-flow distributors must aim for uniform distribution across the entire cross-section of the resin bed, and yet avoid excessive interference with movement of the compacted resin bed during pulsing. The excess capacity indicated by the calculation above, combined with the fact that the concluding runs during the pilot plant optimization study were at 2.5 l/hr., should be more than adequate provision for the uncertainties of scale-up.

A square tower of structural steel was intended to support the resin loop, and provide mounting supports for all auxiliary equipment, such as tanks, pumps, piping, and valves. This tower would also include several grating platforms to provide access to the entire length of the resin loop. Since the overall height of the tower was approximately 47', some provision for

housing and weather protection was necessary. Therefore, the support tower was designed large enough to completely enclose all fittings and connections to the contactor, and to provide space for an access ladder to each of the platform levels. Since appropriate wind loading factors were considered, sheet metal siding and a roof can be applied directly to the support structure, forming a convenient enclosure.

It is planned that the existing 35% waste acid storage tank be used as a source of feed to the recovery system. Figure 3 shows the intended layout of the recovery system and associated tanks adjacent to this existing storage tank.

Upon completion of the engineering plans for the complete recovery system, firm quotations were obtained on all of the rerequired materials and equipment, as well as the necessary labor for assembly and welding of the stainless steel resin loop, and the support tower. It is intended that the support tower be constructed in modules, which can readily be stacked and connected on site, so as to minimize the field erection time and labor. Quotations were also received from contractors in the Cleveland, Mississippi area for the erection, siding installation, and piping and electrical connection work. Table 6 itemizes the various items of capital cost, and indicates the total investment required to have a completely operational phosphoric acid recovery system. The costs associated with conducting, and report on, the demonstration project are not included in this listing, since they have no influence on the economics of the recovery scheme.

Calculations on the economic feasibility of the proposed recovery process can be based on either the total capacity for the 24" unit--1,752 gallons (6,624 liters) per day--or on the present quantity of water--1,350 gallons (5,110 liters) per day. The former approach is applicable, since a second, parallel anodizing line is being installed, so that sufficient waste phosphoric acid will be available to fully utilize the capacity of the recovery system. Thus, at this higher rate of feeding the 35% waste acid, 6,500 lbs. (2,954 Kg) of H_3PO_4 will be fed to the contactor per day. Based on a very conservative 75% recovery of the feed acid, 4,875 lbs. (2,216 Kg) of H_3PO_4 will be fed to the evaporator for concentration into 448 gallons (1,696 liters) per day of 80% phosphoric acid. The plant is currently paying $218.40/ton for 80% phosphoric acid solution, giving the 3.04 tons of recovered solution a value of $664.00 per day, or $166,000 per year.

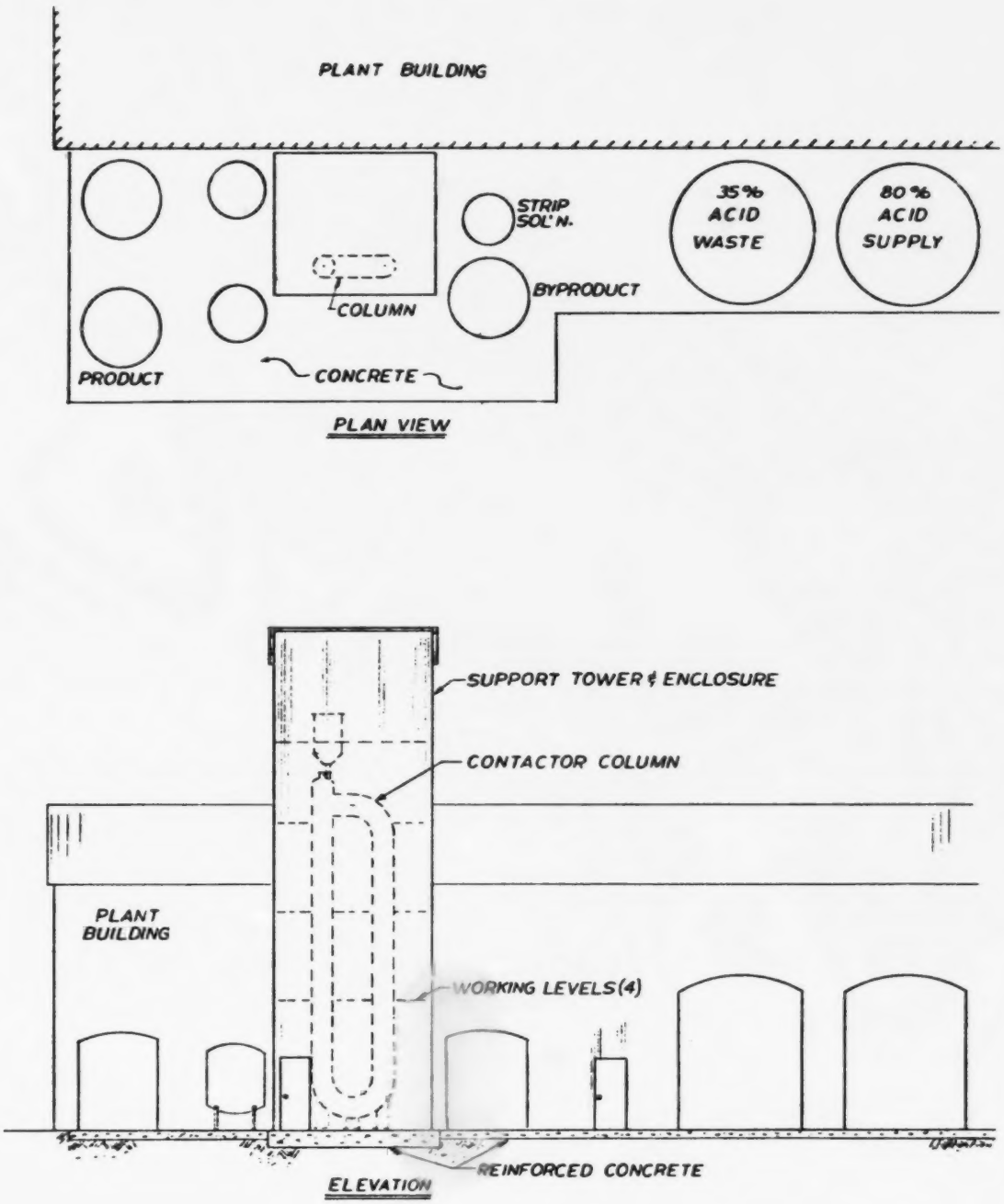

Figure 3. General Arrangement of Recovery System

Table 6

Summary of Capital Costs

1.	Equipment - Contactor Resin Loop. . . .	$ 37,166	
	Support Structure	19,049	
	Pipe and Fittings	5,805	
	Pumps	16,327	
	Valves.	39,023	
	Tanks	17,884	
	Control System.	16,106	
	Miscellaneous	14,950	
	Evaporator.	33,630	$ 199,940
2.	Supplies - Resin, 210 ft.^{3} - Dowex SBR-P		13,230
3.	Installation* - Site Preparation and Erection.	$ 9,000	
	Building Construction and Siding Installation. . .	7,000	
	Piping and Electrical Installation	12,000	28,000
4.	Engineering Services - System Design. .	$ 35,000	
	Start-up Supervision. . . .	7,800	42,800
	Total Invested Capital		$ 283,970

*The installation cost figures are estimates based upon actual quotations from local contractors. They are, of course, subject to some variation, but are considered conservative.

In many cases, waste treatment costs will be reduced by recovery and reuse of the bright dip drag-out. Associated with the recycle of 4,875 lbs. (2,216 Kg) of acid are savings of 2.76 tons (2.5T) per day of lime required for neutralization. This amounts to an annual savings of $15,180 at $22.00 per ton. Furthermore, sludge handling costs of approximately $38,500 per year are avoided, based upon 7,700 gallons (29.2 m^3) per day of slurry containing 10% dry solids, and handling costs of 2¢/gallon. Adding these savings in waste treatment costs gives a total return value of $204,500 per year.

Table 7 lists the various items of operating cost for the recovery system, and indicates a total annual operating cost of $11,905 per year. This gives a net recovery value of $192,595 per year, allowing amortization of the investment capital in approximately 1.5 years.

As mentioned earlier, the Cleveland, Mississippi plant presently collects their recovery rinse overflow and has the 35% acid hauled away by the supplier of the fresh acid. This is a rather common practice for the larger aluminum bright dipping operations. Because of equipment failures and/or operator mistakes, the value obtained with this approach inevitably falls short of the calculated amount. In 1973 the plant received a credit of $32,760 for return of the by-product. Adjustment of the 1973 plant capacity to a production level corresponding to full contactor capacity would give a projected return value of $42,515/year.

The preceding calculations are all based simply upon the value of the phosphoric acid and the associated waste treatment costs and ignore several other significant savings which will accrue because of reduction in the overall operating costs of the anodizing plant. These are due to the fact that the recovery rinses may be run considerably faster with the in-house recovery system than with the haul-away approach. While a nominal figure of 35% has been referred to as the strength of the contactor feed acid, the sorption process can work effectively with a feed of considerably lower acid concentration. The pilot plant operating data given in Table 5 were obtained with a feed stream of 26-27%, and very little efficiency will be sacrificed by going to even lower concentrations.

By running the recovery rinses at a higher rate, the following advantages are realized:

Table 7

Estimated Direct Annual Operating Costs

1.	Personnel - Operator - 2 hrs./day, 250 days @ $6/hour.	$ 3,000	
	Maintenance - 5 hrs./week, $6/hr.	1,872	$ 4,872
2.	Supplies - Resin - 42 $ft.^3$ @ $63.00/$ $ft.^3$		2,646
3.	Utilities - Electric - 22.4 KW, 24 hrs./day 250 days, 1.0¢/KW hr..	$ 1,344	
	Fuel for Heating - 15 Boiler Horsepower, 250 days, 24 hrs./day	3,043	4,387
			$ 11,905

1. The amount of acid dragged out of the final recovery rinse into subsequent fast-flowing rinses is reduced, resulting in less loss and more recovery of acid value. For example, at a production rate corresponding to full contactor capacity, running the recovery rinses to give a concentration of 25% instead of 35% will result in recovery of approximately 72.3 tons (65.6T) per year more acid, with a value of $15,790.

2. Since waste treatment will inevitably be required for the subsequent fast-flowing rinses, the savings of acids mentioned in (1) above will also result in savings of 81.9 tons (74.3 T) per year of lime, with a value of $1,800 and will eliminate the handling of 228,700 gallons (865,630 liters) per year of sludge, saving an additional $4,574 per year. Thus, the total acid and waste treatment savings due to faster flow in the recovery rinses are $22,164 per year.

3. A major problem in producing high-quality anodized parts is the build-up of phosphate ion in the anodizing bath, since it interferes with subsequent sealing operations and reduces the corrosion resistance of the surface. A typical maximum concentration permitted in the bath by automotive specification is 1,000 mg/l. Carry-over of phosphate from the bright dip often causes the anodizing bath to be discarded more frequently than would otherwise be required. Thus, it is obvious that a reduced acid concentration in the recovery rinses can also produce savings in sulfuric acid and lime consumption, as well as sludge handling costs for this secondary waste source. As an example, replacement of a 2,000 gallon (7,570 liter) anodizing bath will cost $75.00 for sulfuric acid, $33.00 for lime, and $40.00 for sludge handling--a total of $148.00, not counting the labor for dumping and preparing the new bath.

4. The work pieces are generally moved rapidly through the recovery rinses to minimize the etching or dulling which takes place when the surface is immersed in dilute phosphoric acid solution. Because of the higher flow rate employed with the recovery system, longer immersion and drainage time can be used, further reducing loss of acid. The product quality can also be appreciably improved.

At full contactor capacity, these additional savings, due to the increased recovery rinse flow rate, may be assumed to be at least $23,000 per year. Adding this to the previously-mentioned acid value ($166,000) gives a total return of $189,000/year. In the comparison with a haul-away approach, this would be reduced by $42,515 of returned acid credit and $11,905 of operating cost, to give a net return of $134,580/year. This would completely return the invested capital in about two years.

One additional factor affecting the economics is the value of the by-product aluminum phosphate/phosphoric acid stream exiting the contactor. Investigations are under way to find the best approach to marketing this material, but since the value has not been firmly established, no credit has been assumed in the foregoing calculations.

More accurate figures will be generated by operation of the prototype unit under actual plant conditions during the second phase of the demonstration project.

SECTION VI

REFERENCES

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